DURIP99 ACQUISITION OF AN OPTICAL PARAMETRIC OSCILLATOR

FINAL REPORT

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A pulsed, tunable optical parametric oscillator system has been acquired in order to carry out spectroscopic studies of weakly bound complexes of the aluminum and other light atoms with hydrogen and other molecules. These data are being used to infer information on the non-bonding atom-molecule interactions in both the ground and excited electronic states.

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ITEMIZATION OF EQUIPMENT PURCHASED

The funds awarded under grant no. F49620-99-1-0100 were used to acquire a Nd:YAG laser pumped optical parametric oscillator system capable of producing high-power narrow-band laser radiation from the ultraviolet into the infrared.

The following specific items were purchased from Continuum, Santa Clara, CA, under this grant:

(1) Powerlite 8000 Q-switched Nd:YAG laser system, 10 Hz

(2) DS-1, TS-1 temperature stabilized second (type I) and third harmonic generators

(3) SPS-2 second and third harmonic outputs when pumping Sunlite OPO

(4) SI-500 injection seeder for SLM operation

(5) SunliteEX visible optical parametric oscillator/amplifier

(6) PS dichroic separation kit (PS-1: 426-491 and 2124-1281 nm; PS-2: 491-581 nm and 1281-910 nm; PS-3: 581-690 nm and 910-730 nm)

(7) FX-1 frequency doubling option for Sunlite OPO system 225-450 nm, includes nonlinear crystals

SUMMARY OF RESEARCH ACCOMPLISHED

The equipment acquired under grant no. F49620-99-1-0100 is being used in the projects described below. Before integrating this laser system into AFOSR-supported work, we chose to break in the system on a relatively undemanding project. The use of the laser system for this project also allowed my group to become familiar with the intricacies of alignment and maintenance of the system. Because of the possibility of damaging the nonlinear BBO crystals in the oscillator and amplifier, we must monitor the Nd:YAG 335 nm third harmonic beam essentially continuously, in order to ensure that the Nd:YAG laser is properly injection-seeded (single-longitudinal mode operation). To ensure that the laser is being operated properly, one student has been designated with primary responsibility for the instrument.

1. Photoacoustic spectroscopy of deuterated methyl halide isotopomers

In NSF-supported work, we have been studying the photodissociation of vibrationally excited methyl chloride and its deuterated isotopomer CHD_2Cl.[1-3] In our initial series of experiments, we investigated the photodissociation dynamics of CH_3Cl and CHD_2Cl excited to their respective fourth C–H stretch overtones [$v_{CH} = 5$]. Ground-state $Cl(^2P_{3/2})$, spin-orbit excited $Cl(^2P_{1/2})$, H, and D atomic photofragments were detected by 2+1 resonance-enhanced miltiphoton ionization in a time-of-flight mass spectrometer. The vibrational excitation of the molecular precursor was monitored by recording the photoacoustic spectrum of the molecules.

The yield of atomic Cl fragments from the vibrationally mediated photodissociation of CHD_2Cl was found to be significantly less than for CH_3Cl, more than could be accounted for from differences in the cross sections for vibrational overtone excitation. This suggests that state mixing leads to a greater amplitude of the wave function of the vibrationally excited level along the dissociation coordinate in CH_3Cl than in CHD_2Cl. This is consistent with the known greater state mixing of the vibrational wave functions of CH_3Cl.[4, 5]

In addition to the primary photochemical pathway of formation of Cl atoms, there is also a minor production of H/D atoms.[2] Unanticipated in our experiment was the observation that D atoms are preferentially formed over H atoms in the photodissociation of $CHD_2Cl(v_{CH}=5)$, despite the fact that the initial excitation is in the C–H bond. This may be explained by the C–H/C–D interbond coupling deduced in a model of the vibrational energies.[5]

We would like to extend these experiments to investigate the photodissociation of lower C–H stretch vibrational levels of these and other methyl halides. With the help of a summer undergraduate student (Kristen Mulherin, Carleton College), who synthesized the CH_2DCl isotopomer, we recorded photoacoustic spectra from excitation of $v_{CH} = 3$ and 4 of CH_3Cl, CH_2DCl, and CHD_2Cl. The requisite wavelength regions for these transitions were conveniently accessed with the optical parametric oscillator. We plan to investigate the photodissociation of these lower excited vibrational levels after rebuilding the time-of-flight mass spectrometer with an imaging detector.

2. Fluorescence excitation spectroscopy of Al–H_2 and Al–N_2 complexes

Our main experimental efforts with this newly acquired optical parametric oscillator system have been to extend our spectroscopic investigations of van der Waals complexes of the aluminum atom with H_2 and also N_2. In our ongoing AFOSR-supported project funded through grant no. F49620-98-1-0187, we have been carrying out spectroscopic studies to characterize the non-bonding interactions of the aluminum atom.

Aluminum atoms are generated in a free-jet supersonic expansion through 193 nm photolysis of trimethylaluminum added to the beam seed gas mixture. Aluminum atoms and complexes are detected downstream by laser fluorescence excitation in the wavelength range around Al atomic transitions. Our laboratory is the first and thus far the only lab to detect the Al–H_2 complex[6] and other Al atom – molecule complexes[7] [Al–N_2 [8] and Al–CH_4 [9]]. We have employed a unique detection scheme suitable for laser fluorescence detection. In an electronically excited atom–molecule complex and in contrast to atom–rare gas binary complexes, we can anticipate that there will be a high probability that the excited state will decay by predissociation through coupling with lower potential energy surfaces. We have succeeded in detecting Al atom–molecule complexes by excitation to excited electronic states higher than the lowest [Al(4*s*)–M here]. In this case, the transition can be detected even if predissociation occurs so long as the final state is an emitting excited state.

With this excitation and detection scheme, we have observed transitions from the ground vibronic level of the Al–H_2 complex to bound vibrational levels of Al(5*s*)–H_2.[6] These transitions were observed both by detection of emission from lower Al atomic states (4*s*, 3*d*) and chemiluminescence of AlH($A\,^1\Pi$) product formed through reaction within the complex. Resonance fluorescence from excited Al(5*s*)–H_2 levels was very weak. From the relative intensities for formation of the various emitting products and the estimated decay rate of the $5s \rightarrow 3p$ transition, the excited-state lifetime was estimated to be ≤ 35 ps.

In more recent experiments employing the optical parametric oscillator, we have been carrying out both laser fluorescence excitation and depletion experiments in order to observe other electronic transitions of the Al–H_2 complex. The fluorescence depletion experiments involve the use of two laser systems, here the optical parametric oscillator system and a Nd:YAG laser pumped dye laser system acquired through a previous DURIP grant [AFOSR grant no. F49620-95-1-0057].

We have succeeded in observing vibrational bands associated with the $3d \leftarrow 3p$ transition of the Al–H_2 complex. Initial observation was achieved by fluorescence excitation, monitoring emission from the Al(4*s*) state. We have also succeeded in observing this transition by fluorescence depletion, with the probe laser tuned to the $5s \leftarrow 3p$ transition. This provides unambiguous proof that these transitions involve the same molecular carrier and gives good assurance that the relative intensities in the spectra are representative of the absorption line strength factors. The pattern of the vibrational levels is complicated and probably reflects the fact that there are 5 potential energy surfaces correlating with the Al(3*d*) + H_2 asymptote.

For some of the bands, the Lorentzian broadening is sufficiently small that rotational resolution has been achieved. The rotational structure in the $3d \leftarrow 3p$ transition is found to be quite different to that observed in the $5s \leftarrow 3p$ transition. Analysis of the rotational structure of this and other electronic transitions may provide clues to a full rotational analysis. The rotational constants and parity splittings determined from such an analysis offers significant information about the complex, such as the average Al–H_2 separation and the energies of low-lying electronic states. We find that the rotational line widths vary for the vibrational bands associated with the $3d \leftarrow 3p$ transition, in some cases sufficiently broad that the rotational structure is completely obscured..

The $4p \leftarrow 3p$ transition is electric-dipole forbidden in the free aluminum atom. However, this transition becomes allowed in the reduced-symmetry environment of an Al atom – molecule complex. We have also observed an electronic transition in the Al–H_2 complex in the spectral region around the $4p \leftarrow 3p$ excitation energy. As with the $3d \leftarrow 3p$ transition, rotational lines within some of the vibrational bands are found to be quite narrow [FWHM < 0.5 cm^{-1}]. We are presently engaged in fully characterizing these and other electronic transitions in the Al–H_2 complex. In order to provide further information to aid in the analysis of the spectra, we will also record spectra of the Al–D_2 isotopomeric complex. In other work, we have observed the $3d \leftarrow 3p$ electronic transition in the Al–N_2 complex.

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